

Unusual structure of an *N*-phosphoryl-*N'*-isopropylthiourea chelate with the nickel(II) cation

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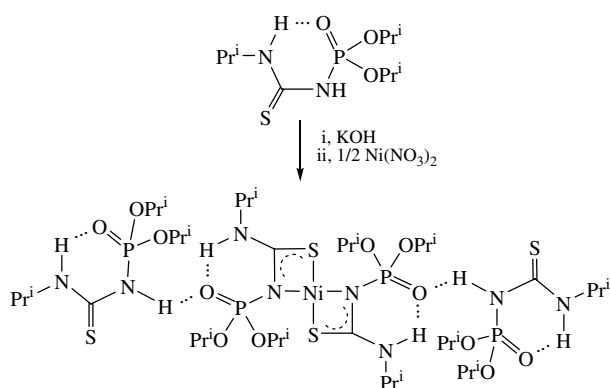
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The reaction of the potassium salt of *N*-phosphorylated thiourea $\text{Pr}^i\text{NHC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2$ (HL) with the Ni^{II} cation leads to the complex $[\text{NiL}_2(\text{HL})_2]$; according to X-ray analysis, two neutral HL molecules are coordinated in the second sphere of the planar 1,3-*N,S*-chelate $[\text{NiL}_2]$ via (HL) $\text{PNH}\cdots\text{O}=\text{P}(\text{NiL}_2)$ hydrogen bonds.

The competitive coordination¹ of polyfunctional ligands with metal cations is of interest in modern coordination chemistry. Recently, we found that *N*-phosphorylthioureas $\text{RNHC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2$ ($\text{R} = \text{Ph}$, cyclohexyl) can form 1,3-*N,S*-chelates with Ni^{II} , Pd^{II} and Cu^{II} cations.² The 1,5-*O,S*-coordination of such a type of ligands³ is not favourable in these cases due to higher crystal field stabilization energies for the square-planar d^8 and d^9 complexes $[\text{M}\{\text{RNHC}(\text{S})\text{NP}(\text{O})(\text{OPr}^i)_2\text{-N,S}\}]$ caused by stronger ligand field of the amide N atom in comparison with the $\text{P}=\text{O}$ oxygen atom. The second stabilising factor for 1,3-*N,S*-chelates is the formation of intramolecular $\text{NH}\cdots\text{O}=\text{P}$ hydrogen bonds.

The synthesis of a Ni^{II} complex with thiourea $\text{Pr}^i\text{NHC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2$ (HL) has led to an interesting result: light violet crystals corresponding to the stoichiometry of $[\text{NiL}_2(\text{HL})_2]$ **1** were isolated from the reaction mixture.[†] The crystals are readily soluble in benzene and chlorinated alkanes and insoluble in water and *n*-hexane. The stoichiometry of complex **1** is preserved after multiple crystallizations from benzene and dichloromethane.



Scheme 1

[†] Thiourea HL was prepared according to the previously described method.⁵ *Synthesis of $[\text{NiL}_2(\text{HL})_2]$* : a suspension of HL (1.410 g, 5 mmol) in aqueous ethanol (20 ml) was mixed with an ethanol solution of potassium hydroxide (0.28 g, 5 mmol). An aqueous (20 ml) solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.815 g, 2.8 mmol) was added dropwise with vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for 5 h and left overnight. The resulting complex was extracted with CH_2Cl_2 , washed with water and dried with anhydrous MgSO_4 . The solvent was removed *in vacuo*. The precipitate was isolated from CH_2Cl_2 by *n*-hexane.

Spectral analyses[‡] and X-ray data[§] undoubtedly indicate the 1,3-*N,S*-type of coordination by two anionic ligand molecules in this case (Scheme 1). Only the examples of 1,5-*O,S*-coordination of the thiourea HL in $[\text{ML}_2]$ chelates with cobalt(II)⁴ and zinc(II)⁵ cations have been reported earlier.

One could presume that complex **1** should contain a six-coordinated Ni^{II} cation. Indeed, such a type of the square-bipyramidal complexes $[\text{M}(\text{QH})_2\text{Q}_2]$ of thioamide $\text{PhC}(\text{S})\text{NHP}(\text{O})(\text{OPr}^i)_2$ (HQ) with Ni^{II} and Co^{II} cations was isolated and investigated by X-ray analysis.⁶ The $[\text{Q}^-]$ ligands in these complexes exhibit a 1,5-*O,S*-coordination with the central ion in the equatorial positions of the bipyramide, while neutral ligands [HQ] are coordinated *via* oxygen atoms of the phosphoryl group in axial positions.

However, the unusual 1,3-*N,S*-coordination of the thiourea ligand $[\text{L}^-]$ leads to interesting changes in complex structure. X-ray analysis has clearly shown that neutral ligands in adduct **1** do not interact directly with the metal ion and being in the second sphere interact *via* hydrogen bonds between the $\text{P}(\text{O})\text{NH}$ protons of free ligands and the $\text{P}=\text{O}$ oxygen atoms of coordinated ligand (Figure 1). The strong ligand field of 1,3-*N,S*-coordinated thiourea moieties, stabilising the square-planar low-spin complex species, does not allow the axial coordination of the HL molecules.

[‡] The IR spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1} . The NMR spectra were obtained on a Varian Unity-300 NMR spectrometer at 25 °C. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to SiMe_4 (^1H) and H_3PO_4 ($^{31}\text{P}\{^1\text{H}\}$). The mass spectra were measured on a TRACE MS Finnigan MAT instrument. The electron ionisation energy was 70 eV. The substance was injected directly into the ion source at 150 °C. Heating was carried out in a programmed mode from 35–200 °C at a rate of 35 K min^{-1} . Elemental analyses were performed on a Perkin-Elmer 2400 CHN micro-analyser.

For $[\text{NiL}_2(\text{HL})_2]$: yield 0.784 g (53%), mp 82 °C. ^1H NMR (CDCl_3) δ : 1.16 (d, 12H, Me $[\text{Pr}^i\text{N}, \text{L}]$, $^3J_{\text{HH}}$ 6.5 Hz), 1.33–1.47 (m, 48H, Me $[\text{Pr}^i\text{O} + \text{Pr}^i\text{N}]$), 1.58 (d, 12H, Me $[\text{Pr}^i\text{O}, \text{L}]$, $^3J_{\text{HH}}$ 6.2 Hz), 3.91 (d sept., 2H, $[\text{NCH}, \text{L}]$, $^3J_{\text{CHCH}}$ 6.5 Hz, $^3J_{\text{CHNH}}$ 8.2 Hz), 4.53–4.72 (overlapped m, 10H, $[\text{NCH} + \text{OCH}]$), 6.86 (br. s, 2H, $[\text{NHP}, \text{HL}]$), 8.33 (d, 2H, $[\text{NHPr}^i, \text{L}]$, $^3J_{\text{CHNH}}$ 8.2 Hz), 10.36 (br. s, $[\text{NHPr}^i, \text{HL}]$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ : –3.8 (HL), 2.9 (L). IR (ν/cm^{-1}): 1016 (POC), 1200 ($\text{P}=\text{O}$), 1560 (SCN), 3176, 3232 (NH). EI-MS, m/z (%): 621 (5) $[\text{M} - 2\text{HL}]^+$. Found (%): C, 40.59; H, 7.60; N, 9.42. Calc. for $\text{C}_{40}\text{H}_{90}\text{N}_8\text{O}_{12}\text{P}_4\text{S}_4\text{Ni}$ (1184.39) (%): C, 40.51; H, 7.65; N, 9.45.